

IDENTIFICATION OF THE HETEROATOM CONTAINING COMPOUNDS IN THE BENZENE/METHANOL EXTRACTS OF THE ARGONNE PREMIUM COAL SAMPLES

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The Argonne Premium Coal Samples (APCS) provide a unique opportunity to study a set of pristine samples specifically selected to represent the vast diversity of chemical structures exhibited by U.S. coals. The purpose of this paper is to utilize high resolution mass spectrometry (HRMS) to characterize the heteroatom containing species that can be extracted from the APCS. Of special interest is the change in structure and relative concentrations that these compounds undergo with rank. The resulting information is important in providing basic chemical structural information concerning these coals which are being used by a significant portion of the coal community, and understanding the transformations that the heteroatom containing species undergo during the coalification process.

EXPERIMENTAL

The coals used in this study and their elemental analyses are presented in Table I and the preparation of the coals has been described in detail by Vorres and Janikowski¹. The sample handling and extraction procedures along with an overview of our overall analysis scheme have been presented previously².

Table I. Elemental analysis of the APCS coal samples used in this study.

APCS Number	Coal	Carbon	Hydrogen	Nitrogen	Sulfur _{org}	Oxygen _{diff}	Extract Yield
8	Beulah-Zap	72.9	4.83	1.15	0.70	20.34	2.0
2	Wyodak Anderson	75.0	5.35	1.12	0.47	18.02	5.3
3	Illinois #6	77.7	5.00	1.37	2.38	13.51	8.2
6	Blind Canyon	80.7	5.76	1.57	0.37	11.58	7.5
7	Lewiston-Stockton	82.6	5.25	1.56	0.65	9.83	3.1
4	Pittsburgh	83.2	5.32	1.64	0.89	8.83	3.7
1	Upper Freeport	85.5	4.70	1.15	0.74	7.51	0.5
5	Pocahontas #3	91.0	4.44	1.33	0.50	2.47	1.9

However, a brief overview the experimental procedure is appropriate here. One hundred grams of the -100 mesh dried coal was extracted for 48 hours in 250 ml of boiling benzene/methanol azeotrope (40/60 w/w percent). The extract was removed by vacuum filtration, the residue was washed with 50 ml. of the azeotrope, and dried to constant weight at 100°C under vacuum. The two low rank coals (Wyodak Anderson and Beulah Zap) were extracted without drying in order to avoid irreversible physical or chemical changes that are known to occur during drying. The azeotrope was stripped from the extract at 70°C under vacuum in a rotary evaporator and the extract brought to constant weight. The two higher rank coals (Upper Freeport and Pocahontas #3) did not yield enough extract for subsequent separation.

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The extract from the six lower rank coals was then separated into nine fractions using the desorption column chromatographic technique (DSEC) developed by Farcasiu¹⁴. The elutants in order of use include: (1) hexane, (2) hexane/15% benzene, (3) chloroform, (4) chloroform/10% diethyl ether, (5) diethyl ether/3% ethanol, (6) methanol, (7) chloroform/3% ethanol, (8) tetrahydrofuran, (9) pyridine/3% ethanol. In our application of this technique the extract was dissolved in 7 ml. of the azeotrope and coated on 6.65 grams of dried silica gel by rotary evaporation of the solvent. The coated silica gel was placed on the top of the column containing 26.8 grams of Aldrich Grade 12 silica gel. This silica gel had been dried for 8 hours at 120°C and then rehydrated to 4 percent water. Blank elutions were performed in order to correct the weight of each fraction for dissolved silica gel.

For the high resolution mass spectra approximately 20 mg. of the extract from fractions 3-6 was dissolved in benzene/methanol azeotrope. 0.1 mg of the Diels-Alder adduct of D₁₀-anthracene and maleic anhydride was added as an internal standard and the resulting solution concentrated to 0.3 ml. The synthesis and applicability of this adduct as an internal standard in HRMS has been discussed previously⁷. The solution was placed on the tip of a glass probe and the solvent was allowed to evaporate. The probe containing the sample was inserted into the all glass inlet system held at room temperature and evacuated. The temperature of the inlet system was rapidly raised to 350°C and the volatilized sample was allowed to leak into the source of the Kratos MS 50 high resolution mass spectrometer. Approximately 10 scans were obtained for each sample at an electron ionization energy of 70 eV, and a scan rate of 100 seconds/decade providing a dynamic resolution of 40,000. The resulting data was transferred to a Micro Vax II for final analysis. This analysis utilized a set of programs developed in house for averaging the scans in the run and assignment of elemental formulae to the averaged masses and sorting by heteroatom content and hydrogen deficiency (HD = rings + double bonds)⁶.

RESULTS AND DISCUSSION

The distribution of the extract in each of the DSEC fractions, for each of the coals for which enough extract was available, is shown in Figure 1. Although, no strict correlations are observed, several general conclusions can be drawn. The percentage of the total extract eluting in the hexane (1) and chloroform/10% diethyl ether (4) - Tetrahydrofuran (8) fractions tends to decrease with rank while the hexane/15% benzene (2) and chloroform (3) fractions increase. This is not particularly surprising since we know from elemental analysis that the amount of oxygen decreases with rank⁷ while the nitrogen content remains steady or increases only slightly⁸. Yarzab, Given and coworkers⁹ have shown that the phenolic content decreases with rank. However, a linear correlation is only observed with carbon content within a single coal province. The amount of extract eluting in the hexane (1) fraction shows the tendency to decrease with rank if the Blind Canyon coal is not considered. This coal is unusual in the fact that it exhibits an abnormally high liptinite content. Gas chromatography/mass spectrometry (GC/MS) of this fraction indicates that it is composed almost exclusively of alkanes and cycloalkanes. GC/MS and HRMS of the hexane/15% benzene (2) fraction indicated that only trace amounts of heteroatomic species are present. Thus, the remaining discussion in this paper will be limited to the chloroform (3) through methanol (6) fractions.

The degree of condensation increases with rank for each of the heteroatomic classes of compounds. Figure 2 illustrates this trend using single oxygen containing ions from the chloroform (3) fraction. The two low rank coals (Beulah Zap (#8) and Wyodak Anderson (#2)) are dominated by species with HD values less than 10. An HD of 10 corresponds to an anthracene or phenanthrene type structure if all of the rings are aromatized. A more likely assignment would be a smaller condensed structure with additional aliphatic or partially unsaturated rings. While the higher rank coals exhibit much larger contributions from ions with HD values in the range of 10-19. For the two highest rank coals for which we have data (Pittsburgh (#4) and Lewiston-Stockton (#7)), a maximum in the distribution is observed at HD=12. This corresponds to the empirical formula C₂₀H₁₈O for the base structure of the homologous series. This trend was also recognized by Given and coworkers who used catalytic dehydrogenation by Pd/CaCO₃ in boiling phenanthridine.¹⁰

Oxygen Compounds. Compounds containing one, two and three oxygens are present in the extracts from all of the coals. The distribution of these classes among the fractions are presented in Table II. Single oxygen containing species are found primarily in the chloroform (3) and chloroform/10% diethyl ether (4) fraction, two oxygen containing species in the chloroform/10% diethyl ether (4) and diethyl ether/3% ethanol (5) fractions, and three oxygen containing species in the methanol (6) fraction. Single oxygen carbonyl compounds of the type

investigated by Given and Peover¹¹ may also be present in this fraction. However, their unequivocal identification by HRMS is not possible.

The single oxygen compounds in the chloroform (3) fraction appear to be primarily phenolic in nature with maxima at HD 4, 7, and 10. While those in the chloroform/ether fraction produce a higher concentration of ions at HD= 3, 6, 9 which can be assigned to structures containing five membered rings or those containing several aliphatic or partially saturated six member rings. Since compounds of these two types are isomers it is not possible to distinguish between them by HRMS. An example of the HD distribution for these compounds was presented in Figure 2 above.

The two oxygen containing compounds which are found in every fraction are predominantly aliphatic carboxyl based (HD=1) for the low rank coal and dihydroxy or furan based for the coals of higher rank. The carboxyl containing compounds were found in each of the fractions for the lower rank coals but primarily in the methanol fraction (6) for the higher rank coals. The fragmentation pattern of the carboxyl compounds eluting in the less polar fractions indicate that they are most likely esters. These esters which were also observed by Bockrath et al.¹² could be either indigenous to the coal as suggested by Niwa et al.¹³ or formed during the extraction in benzene/methanol. This contradicts the work of Miller et al.¹⁴ who claimed that acids were present only lignites, low rank subbituminous and a few Rocky Mountain H₂C bituminous coals. In the low rank coals carboxylic acids are observed with carbon numbers up to 33 while in the higher rank coals the series ends at 6 carbons.

The three oxygen containing compounds appear primarily at HD= 4, 7, 10 which corresponds to fully aromatized compounds with three OH groups. However, the base compound is not found in the series from any of the coals. This leads to the conclusion that instead of being purely phenolic in nature the three oxygen compounds eluting in this fraction are at least partially alkoxy in nature. This is not surprising since purely phenolic three oxygen containing compounds would be very difficult to elute. Somewhat surprising is the amount of aliphatic, and partially unsaturated (HD<4) three oxygen compounds that are found in the methanol fraction. These compounds make up from 17 to 40 percent of all of the three oxygen compounds eluting in this fraction. The difficulty in rationalizing the presence of possible structures for these compounds in coal leads to the possibility that they are either contamination or mis-assignments.

Nitrogen Compounds. Single and double nitrogen containing species eluted primarily in the methanol (6) fraction, but trace amounts of one single nitrogen containing compounds were also observed in the chloroform (3) fraction. In the chloroform (3) fraction three series of alkylated condensed anisoles are present at HD= 6, 9, and 12 for the higher rank coals. Probable structures for these compounds include either the N, or highly hindered C, alkylated forms. Although a definitive conclusion can not be drawn, the discreteness of elution with

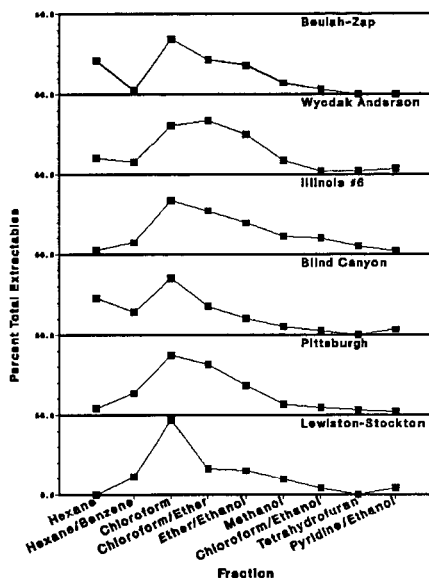


Figure 1. Distribution of the total extract in each of the DSEC fractions.

two interleaving fractions before the next appearance of compounds exhibiting the same elemental formula, leads to the conclusion that these are the N alkylated forms, as has been proposed previously¹⁵.

The ratio of HD=9/10 and 12/13 is plotted versus carbon content in Figure 4. Except for Illinois #6 coal the ratio decreases with rank. The interpretation of this figure is somewhat complicated by the fact that it is impossible to distinguish if the nitrogen is in the 5 membered ring or not. The plot does show that the relative degree of aromaticity increases with rank. Species containing two nitrogen compounds are present in the extract from all of the coals except Beulah Zap. The most prominent series of these compounds is found at HD=9. A series based on a second compound would have as its base the formula $C_{11}H_8N_2$, which was not observed. This corresponds to the formula $C_{12}H_{10}N_2$ for the base compound.

Sulfur Compounds. All of the extracts contained minor amounts of thiophenic compounds (HD= 6, 9, 12) which eluted in the ether/3% ethanol (5) fraction. Although sulfur is notoriously difficult to identify in HRMS, the small deviations from the expected mass, the generation of rational structures for annulated thiophenes versus irrational structures for alternative classes of compounds, and the observance of the expected HD distribution lead to the conclusion that the assignments are valid. The assignment of sulfur containing structures to possible matches at HD values other than those corresponding to thiophenes would be considerably more tenuous, due to the failure of at least two of the criteria mentioned above.

Mixed Heteroatomic. The mixed heteroatom containing compounds are found primarily in the diethyl ether (5) and methanol (6) fractions. The most prominent species from all of the coals are the hydroxylated pyridines, indoles and their higher order annulates. These compounds follow the same trend (see Figure 5) as that observed for the unhydroxylated indoles and pyridines, showing a decrease in the ratio of the 5 membered ring to that of the 6 membered ring with rank. A significant number of sulfur-nitrogen compounds may also be present in the methanol (6) fraction of the higher rank coals. These compounds are observed primarily at HD = 3, 4, 6, 7, 9, 10, 12, 13. However, as mentioned in the previous paragraph, compounds containing sulfur are notoriously difficult to assign structure due to their small mass defect. Hydroxylated thiophenes were not observed in any of the fractions.

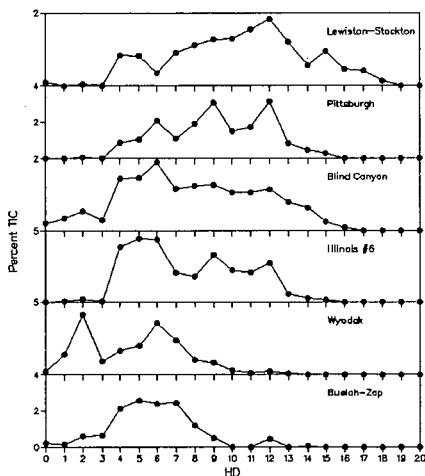


Figure 2. Variation in HD for single oxygen containing compounds in the chloroform (3) fraction.

Table II. Variation of one two and three compounds in DSEC fractions 3-6.

Coal	Chloroform (3)			Chloroform/10% Diethylethe (4)		
	One O	Two O	Three O	One O	Two O	Three O
Beulah Zap	13.2	2.7	0.0	15.3	1.0	0.1
Wyodak-Anderson	18.8	14.4	0.2	20.3	21.5	2.1
Illinois #6	28.3	2.4	1.5	33.9	6.4	1.4
Blind Canyon	14.8	2.2	0.3	12.2	12.4	1.9
Pittsburgh	18.1	0.3	4.0	50.1	5.0	2.7
Lewiston-Stockton	13.9	1.1	4.0	30.2	12.2	2.1

Coal	Diethyl Ether/3% Ethanol (5)			Methanol (6)		
	One O	Two O	Three O	One O	Two O	Three O
Beulah Zap	22.1	14.0	4.0	13.7	12.6	2.8
Wyodak-Anderson	19.0	21.9	5.5	12.3	11.7	4.8
Illinois #6	12.3	4.9	1.2	3.6	1.0	12.7
Blind Canyon	11.5	11.3	7.6	2.9	2.1	11.3
Pittsburgh	19.2	13.7	5.7	7.3	4.3	9.8
Lewiston-Stockton	11.3	8.3	4.8	5.6	1.6	9.4

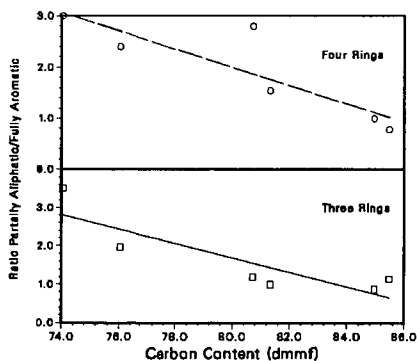


Figure 3. Ratio of HD 9/10 and 12/13 for the single nitrogen containing species in the methanol (6) fraction.

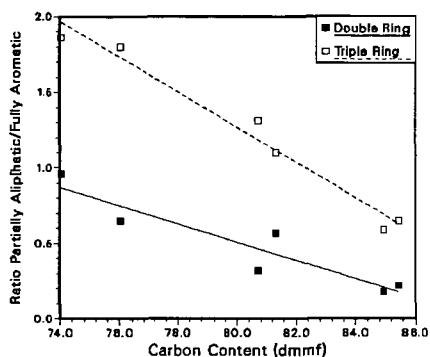


Figure 4. Ratio of HD 9/10 and 12/13 for the oxygen-nitrogen containing compounds in the methanol (6) fraction.

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